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14. ABSTRACT
We have developed approaches towards the goal of producing material on-scale while still enabling selection of the optimal affine compound from the entire chemical space of well over 1012 sequences. Specifically, we have implemented two unique, stand-alone approaches for novel material design and synthesis that both will enable the sequence-specific selection and formation of a high yielding affinity compound in a single step. Broadly, these approaches involve (i) the creation of libraries of smaller, oligomeric species that remain reactive, which, when ligated to a template will arrange in a thermodynamically favorable geometry, external stimuli (light in this

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Christopher Bowman
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Report Title

Final Report: Thiol-X Click Foldamers for Polymer Affinity

ABSTRACT

We have developed approaches towards the goal of producing material on-scale while still enabling selection of the optimal affine compound from the entire chemical space of well over 1012 sequences. Specifically, we have implemented two unique, stand-alone approaches for novel material design and synthesis that both will enable the sequence-specific selection and formation of a high yielding affinity compound in a single step. Broadly, these approaches involve (i) the creation of libraries of smaller, oligomeric species that remain reactive, which, when ligated to a template will arrange in a thermodynamically favorable geometry, external stimuli (light in this instance) will covalently couple the small strands into a strongly binding aptamer, and (ii) the creation of polymers with dynamic, rearrangable backbones which have the capacity, when exposed to a template, to dynamically reconfigure sequence – giving access to the entire sequence space associated with random, extended sequences while ideally resulting in high yields of the affine molecules. Both of these approaches are ideally suited for creating affinity compounds for both oligonucleotides and other compounds, but due to their scalability they will certainly have applications in other material pursuits including polymer networks, supramolecular catalysis, and nanomaterials.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
10/14/2015	1.00	Weixian Xi, Sankha Pattanayak, Chen Wang, Benjamin Fairbanks, Tao Gong, Justine Wagner, Christopher J. Kloxin, Christopher N. Bowman. Clickable Nucleic Acids: Sequence-Controlled Periodic Copolymer/Oligomer Synthesis by Orthogonal Thiol-X Reactions, Angewandte Chemie International Edition, (10 2015): 0. doi: 10.1002/anie.201506711
TOTAL:	**1**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
TOTAL:		

Number of Papers published in non peer-reviewed journals:

(c) Presentations

C.N. Bowman, Clicking Polymers Together: Assembly of Complex, Controlled Polymer Structures from Efficient Chemistries" Invited Lectures Presented at Cornell University, High Polymer Research Group Conference, Rensselaer Institute of Technology, Columbia University, Kent State University, University of Houston, University of California Santa Barbara, Pacific Polymer Conference, Zing Polymer Conference

Additional contributed talks have been given at the ACS National Meeting (2) and the Pacific Polymer Conference (1)

Number of Presentations: 12.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Thiol-X Click Foldamers for Polymer Affinity and Catalysis Libraries

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Weixian Xi	0.23	
Chen Wang	0.55	
Hannah Coley	0.00	
FTE Equivalent:	**0.78**	
Total Number:	**3**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Sankha Pattanayak	0.54
Brady Worrell	0.89
Sudhi Mavila	0.11
FTE Equivalent:	**1.54**
Total Number:	**3**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Christopher Bowman	0.00	No
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Justine Wagner	0.00	Chemistry
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Weixian Xi
Chen Wang
Total Number: **2**

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

5 **Thiol-X Click Foldamers for Polymer Affinity and Catalysis Libraries**

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Was the assignment forwarded to the contracting officer? (5e) N
Foreign Countries of application (5g-2): PCT Application Stage - foreign countries to be decided

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5f-1a: University of Colorado
5f-c: CB 596
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5a: Christopher Kloxin
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5a: Weixian Xi
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Boulder CO 80301

5a: Tao Gong
5f-1a: University of Colorado
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Boulder C) 80301

Scientific Progress

See Attachment

Technology Transfer

Click Nucleic Acids Inc. is a start-up focused on the thiol-X click nucleic acids developed in part as a result of this program. This start-up is currently seeking venture funding for its efforts and has purchased options to the intellectual property focused on click nucleic acids originating from the University of Colorado. In particular, the company is seeking funding for the development of approaches to treat trinucleotide disorders such as Huntington's disease.

Thiol-X Foldamers for Polymer Affinity

Final Report

Christopher N. Bowman, Brady Worrell, Chen Wang, Sudheendran Mavila, Benjamin Fairbanks, Sankha Pattanayak, Weixian Xi, Zhenzhen Liu. University of Colorado at Boulder

Foreword: We desired to access 10^{12} distinct polymer molecules at reasonable scales, each with their own sequence, length, and ability to target, bind, and neutralize chemical or biological threats. Generally, conventional approaches rely heavily either on (*i*) a PCR-like approach in preliminary affinity interactions in which replication and amplification of sequences selected in miniscule yields are used to form the desired compound on scale, or (*ii*) a solid-phase synthesis approach of a targeted sequence that often severely limits both the amount of material which can be produced and the maximum length of the sequence. We have accordingly developed approaches towards the goal of producing material on-scale while still enabling selection of the optimal affine compound from the entire chemical space of well over 10^{12} sequences. Specifically, we have implemented two unique, stand-alone approaches for novel material design and synthesis that both will ultimately enable sequence-specific selection and formation of a high yielding affinity compound in a single step. Broadly, these approaches involve (*i*) the creation of libraries of smaller, oligomeric species that remain reactive, which, when ligated to a template will arrange in a thermodynamically favorable geometry, external stimuli (light in this instance) will covalently couple the small strands into a strongly binding aptamer, and (*ii*) the creation of polymers with dynamic, rearrangable backbones which have the capacity, when exposed to a template, to dynamically reconfigure sequence – giving access to the entire sequence space associated with random, extended sequences while ideally resulting in high yields of the affine molecules. Both of these approaches are ideally suited for creating affinity compounds for both oligonucleotides and other compounds, but due to their scalability they will certainly have applications in other material pursuits including polymer networks, supramolecular catalysis, and nanomaterials. The following report addresses progress towards the realization of these two systems during our DARPA funding period. Progress in these areas has and will continue beyond the funding from DARPA as well.

Table of Contents:

List of Schemes, Figures, and Equations:

Figure 1: Illustration of the general CNA-based monomer structure as well as specific motifs that have been synthesized successfully.

Figure 2: MALDI outcome; formation of a random oligomer library.

Figure 3: CNA kinetic results demonstrating control over both conversion (*left*) and molecular weight of the resultant polymer (*right*).

Figure 4: CNA/DNA affinity-directed particle-particle interactions. **A**. TEM image revealing complementary interactions between CNA(polyT) silica nanoparticles and DNA(15A) coated gold nanoparticles. **B**. TEM image reveals lack of interactions between CNA(polyT) modified silica nanoparticles and DNA(10T) coated gold nanoparticles.

Figure 5: A successful on scale route towards a boc-protected thiolactone.

Figure 6: Successful deprotection of the boc-thiolactone, failed amide formation with thymine acetic acid, and the proposed polymeric by-product.

Figure 7: A. The calculated downhill reaction of arylthioesters with alkyl thiols with a minimal kinetic barrier; B. Experimental confirmation of the calculated results by NMR.

Figure 8: A. Condensation polymerization of an AB-type monomer which bears both an alkyl thiol and an aryl thioester; B. GPC and MALDI confirmation of the dynamic polythioester polymer.

Figure 9: Synthetic route towards the formation of an AB-type monomer bearing a thymine, thioester, and a thiol.

Figure 10: Condensation polymerization of the AB-type thymidine analogue with a base catalyst.

Scheme 1: Assembly of CNA-coated quantum dots and DNA coated Au nanoparticles

Scheme 2: Ring opening polymerization of nucleobase appended thiolactones into a functional, dynamic library capable of self-selecting its own affinity compound

Statement of the Problem Studied: As part of the Fold F(x) program we progressed towards formulation of a system which would allow an unskilled practitioner to rapidly screen, sequence, and form a library of functional, non-natural, sequence-defined polymers as affinity reagents or catalysts for targets of interest to the DOD. We utilized thiol-X chemistries (thiol-ene, thiol-Michael, and thiol/thioester exchange) that react virtually quantitatively, rapidly (~seconds), and under ambient conditions, to form the backbone of such linear polymers. Initially we used such thiol-X backbones with appended nucleobases to form sequence controlled polymers for binding; subsequent studies focused on the formation of dynamic polymer backbones with an ability to form in situ libraries.

Summary of the Most Important Results:

As detailed extensively in our previous updates, our first approach towards fulfillment of the program goals concentrates on the use of thiol-X chemistries, specifically thiol-ene and thiol-Michael reactions, to build up large libraries of nucleobase decorated polymers, the key findings and results from this work were in short: (*a*) the formation of a versatile CNA monomer library, (*b*) polymerization and co-polymerization approaches with control over molecular weight, (*c*) the production of sequence-controlled oligonucleotide polymers in solution, and (*d*) the sequence-specific affinity of CNA polymers towards their DNA complements.

a. The formation of a versatile CNA monomer library. Initial efforts focused on development of click nucleic acid (CNAs) monomers capable of undergoing orthogonal thiol-ene and thiol-Michael reactions. Thus far we have produced several backbones decorated with all 4 of the complimentary nucleobases adenine/thymine and guanine/cytosine which can be efficiently polymerized to moderate sized polymers capable of forming >>1012 sequence distinct polymers by either the thiol-ene (radical initiated) or thiol-Michael (base initiated) reactions. Several distinct backbones have been synthesized thus far, as illustrated below (**Figure 1**). Importantly this library contains both A-B monomers (ene/thiol and acrylamide/thiol) and A-A monomers (dithiol and diene). Such a library has many benefits, as such, in the first case, the A-B monomer will allow for the formation of larger polymers by the built in stoichiometry of the functional groups by reaching higher conversions and in the latter case, the A-A monomer will allow for perfect sequence control in the resulting polymer. Key benefits that remain to be realized include (*i*) the need for alternative backbones that facilitate water solubility and enhanced stiffness, (*ii*) libraries of compounds that facilitate sequence-dependent structure and interactions not based on nucloebases hydrogen bonding, and (*iii*) tailored backbones of variable length capable of binding tightly or alternatively loosely binding to DNA.

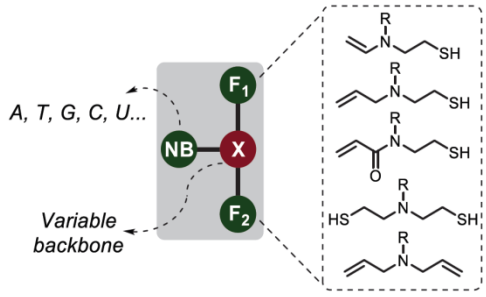


Figure 1: Illustration of the general CNA-based monomer structure as well as specific motifs that have been synthesized successfully.

b. Successful polymerization of CNA monomers and generation of random oligomer libraries. Here, we use the thiol-ene and thiol-Michael reactions to form oligomeric random sequences of controlled length to dictate the strength and specificity of the interactions with the target molecule/template. These oligomers can undergo thermodynamic templation and subsequently, upon the application of an external stimulus, be polymerized *in situ* to form the desired covalently linked high molecular weight affinity compound as informed by the target/template. We have accordingly generated a library of random sequence oligomers via polymerization of nucleobase appended thiol-ene monomers. Naturally, the average composition of the polymer is controlled by varying the relative ratios of the nucleobase monomers; for example, if a library of sequences with predominance of adenine is desired, it may be obtained by a reaction with an initial higher relative concentration of adenine. As shown by MALDI (**Figure 2**), a library generated via photopolymerization of an equimolar mixture of nucleobase monomers. From the spectrum individual trimer and dimer sequences can be identified, which is consistent with a random polymerization of nucleobase monomers. The average degree of polymerization by NMR

end-group analysis was determined to be X_n = 3 (predominantly formation of trimmers) which is consistent with the results noted in the MALDI analysis. Such a degree of polymerization translates to a library of approximately 64 unique compounds.

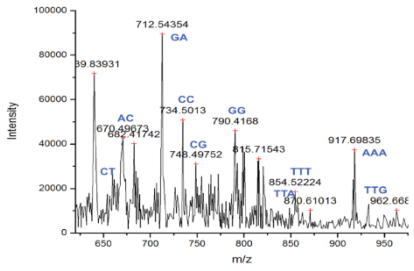


Figure 2: MALDI outcome; formation of a random oligomer library.

While we have aimed for a low degree of polymerization to allow for the more straightforward analysis of the MALDI spectra to verify the random polymerization, oligomers with 10-20 repeat units are regularly obtained with such polymerizations but longer irradiation times. A library corresponding to such a polymerization of random nucleobase monomers would contain 10^6 to 10^{12} unique sequences. Kinetic measurements on a model polymerization have also been explored, demonstrating both the ease with which the functional group conversion and corresponding average degree of polymerization are controlled.

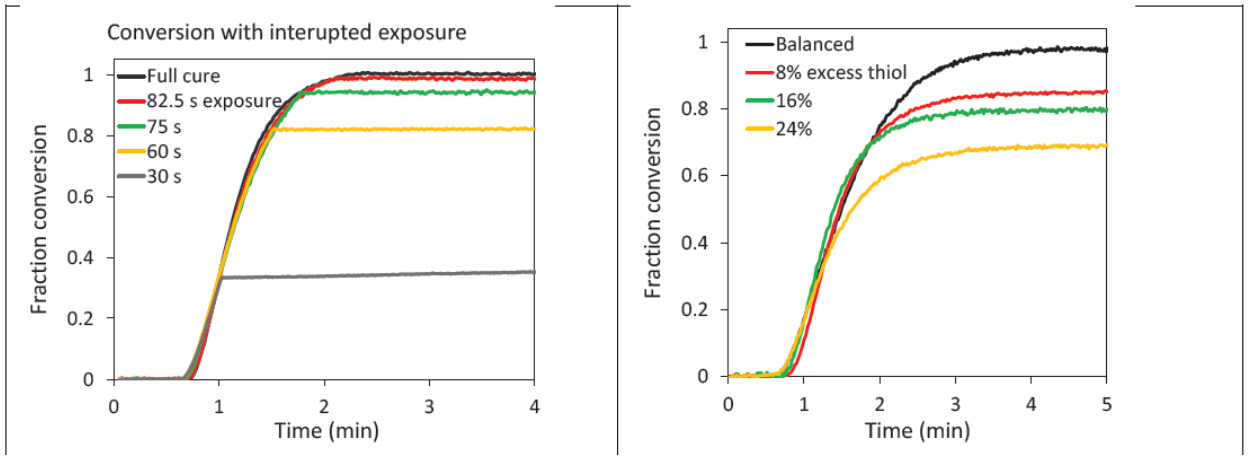


Figure 3: CNA kinetic results demonstrating control over both conversion (*left*) and molecular weight of the resultant polymer (*right*).

c. The sequence-specific affinity of CNA polymers towards their DNA complements. DNA hybridization has frequently been used to direct particle assembly both to reversibly bind together particles of two different characteristics or to selectively surface-pattern such particles through sequence specificity. In fact, with the simpler homopolymer sequences of CNA, hybridization similar to DNA is readily achieved in organic media without for the need of added salt and with a polymer which is readily formed in multigram scales. Specifically, 50 nm of CNA-polyT conjugated silica coated upconverting nanoparticles composed of $NaYF_4$:18% Yb, 2% Er were mixed with DNA-polyA coated gold nanoparticles and incubated together. As shown below (**Figure 4**), TEM imaging revealed abundant conjugation between the silica and gold nanoparticles as directed by the CNA-DNA affinity-based interactions. A control experiment with DNA-polyT coated gold nanoparticles with the CNA-polyT conjugated silica nanoparticles resulted in minimal nonspecific binding of the two nanoparticle types.

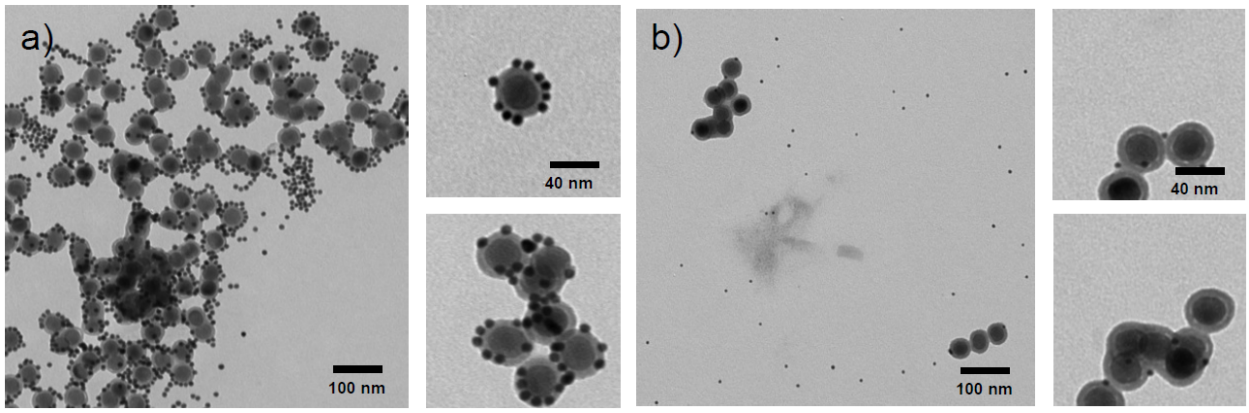
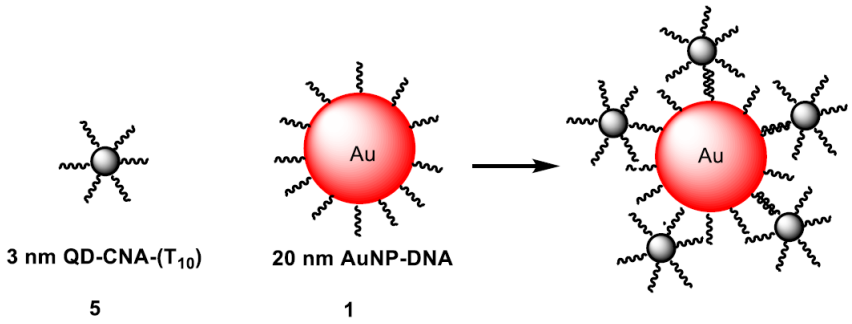


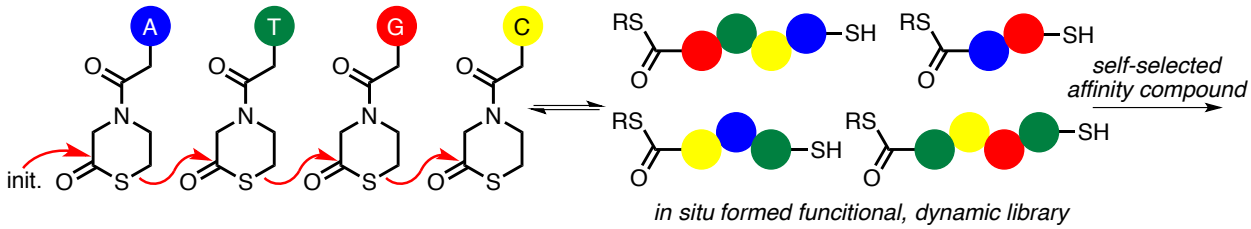
Figure 4: CNA/DNA affinity-directed particle-particle interactions. **A**. TEM image revealing complementary interactions between CNA(polyT) silica nanoparticles and DNA(15A) coated gold nanoparticles. **B**. TEM image reveals lack of interactions between CNA(polyT) modified silica nanoparticles and DNA(10T) coated gold nanoparticles.

Furthermore, the sequence specific assembly directed by CNA/DNA hybridization was also observed between gold nanoparticles and quantum dots, as illustrated below (**Scheme 1**). In analogous control experiments, the mismatched DNA/CNA indicated minimal non-specific binding between gold nanoparticles and quantum dots, while the CNA-labeled quantum dots interacted strongly with the DNA-labeled gold nanoparticles.



Scheme 1: Assembly of CNA-coated quantum dots and DNA coated Au nanoparticles.

d. *Synthesis and ring opening polymerization of nucleobase appended thiolactones towards the formation of dynamic polymers*: As was initially proposed to and funded under this program, we, broadly, intended to develop an approach towards the single step, one-pot synthesis of sequence controlled DNA analogues via polymerization reactions which were both scalable and rapid. Such DNA analogues were anticipated, due to their neutral backbones, highly defined sequences, and 6-membered periodicity to bind tightly to complementary DNA, RNA, or PNA. Specifically, we aimed to reversibly and dynamically polymerize thiolactone monomers in a ROP (ring opening polymerization) bearing nucleic acids to replicate a sequence of complementary DNA, RNA, or PNA strands via thermodynamic constrains (**Scheme 2**). Progress towards realization of this aim via the originally proposed methods, discussion of their failure/setbacks, and new, alternative proposed routes/methods are shown and discussed below.



Scheme 2: Ring opening polymerization of nucleobase appended thiolactones into a functional, dynamic library capable of self-selecting its own affinity compound

Our initial studies focused on synthesizing a boc-protected thiolactone on scale. This began by the monoalkylation of n-benzylethanolamine, hydrogenation of the benzyl group, exposing a secondary amine, and capping of this amine by formation of boc-carbamate. Activation of the alcohol by reaction with methanesulfonyl chloride followed by S_N2-displacement placed all of the desired functionality onto the molecule in protected form. Global basic hydrolysis followed by cyclization at low concentrations afforded the final boc-protected thiolactone in the overall yield of 66% as an odorless, bench stable, yellow solid (**Figure 5**).

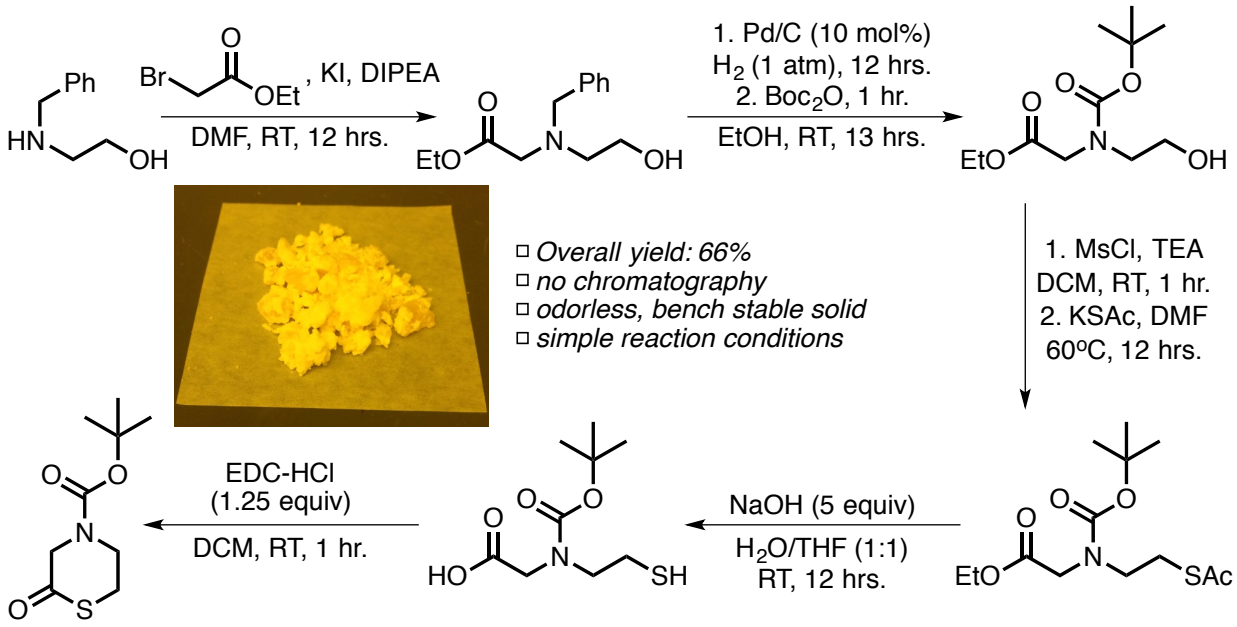


Figure 5: A successful on scale route towards a boc-protected thiolactone.

Ring opening polymerization of the boc-protected thiolactone was possible utilizing 10 mol% initiator and an excess of an amine base; however, low conversions and high PDI were noted. Moving forward, deprotection of the boc group under acidic conditions yielded the hydrochloride salt of the thiolactone quantitatively (**Figure 6A**). Attempted amide coupling of the exposed secondary amine of the thiolactone utilizing thymine acetic acid under various conditions did not yield the desired product, but formed an insoluble polymer; the proposed structure is in **Figure 6B**. Small quantities were isolated (under 10% yield), but synthetically relevant quantities were not obtained. Alternative routes towards such nucleobase appended thiolactones were attempted, including: *i.* utilization of

different acylation conditions; *ii.* coupling of the thymine acetic acid to the exposed secondary amine earlier in the synthesis; and *iii.* altering the structure of the ring to a peptoid-like structure.[2] However, each of these routes failed (either by not yielding the final product or failing to undergo ring opening polymerization), forcing us to devise a new method for formation of a polythioester polymer with appended nucleobases. More information regarding the aforementioned failed routes/polymerizations can be found in any of the attached slides decks.

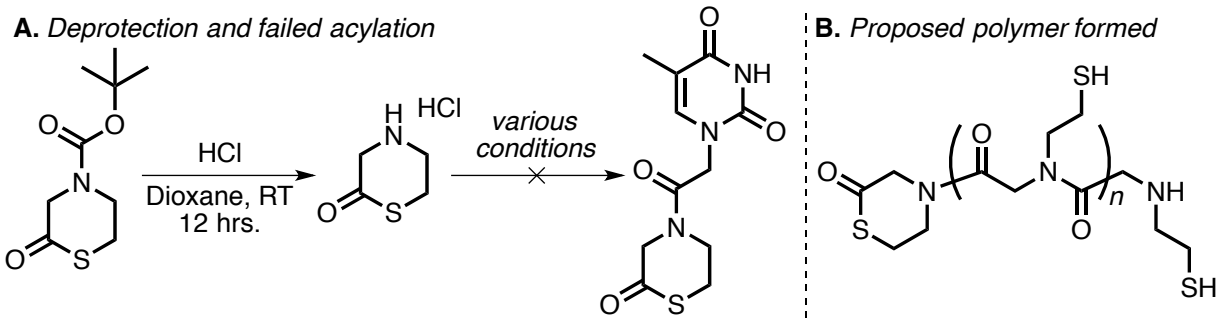


Figure 6: Successful deprotection of the boc-thiolactone, failed amide formation with thymine acetic acid, and the proposed polymeric by-product.

e. *Invention of a novel, robust, and ambient temperature polymerization of thioesters*: We also considered, fundamentally, how polythioester containing polymers could form under mild conditions, in high conversions, with an appended nucleic acid, while retaining their ability to be dynamic during and after polymerization. Simultaneously, a computational finding from another ongoing project in our lab utilizing thioesters as a dynamic functional group significantly aided in identification of a suitable approach. The computational result considered the non-degenerate exchange reaction of a deprotonated alkyl thiol with an aryl thioester (**Figure 7A**). Amazingly, this reaction had an exceedingly low barrier (2.4 kcal/mol, assume ~22 kcal/mol available to any given reaction at room temperature) and was found to be modestly exothermic (-13.6 kcal/mol). We quickly confirmed this computational result by tracking the reaction of methyl mercaptopropionate and S-acylthiophenol in D_6-DMSO with catalytic base (10 mol%, TEA), showing that the reaction did favor formation of products (**Figure 7B**). With this result, we targeted the formation of a nucleobase-functional polymer utilizing the thiol-thioester exchange. This dynamic reaction is well known to occur at extremely low concentrations, in the presence of multiple functional groups, at room temperature, and would be dynamic after and during the reaction; holding tightly to the constraints we sought to fulfill.

We used commercially available Fmoc-Cys(Trt)-OH to form the thioester under conditions pioneered by Mukaiyama (PPh_3/PhSSPh, MeCN, reflux) followed by subsequent acidic deprotection of the thiol (TFA/TES, DCM, RT), yielding our desired "AB" type monomer. Taking this monomer and exposing it to catalytic triethylamine in DMSO yielded the desired polymer in an hour. Existence of the polymer was confirmed by both GPC and MALDI; with MALDI showing the correct repeat unit molecular weight spacing. Amazingly, if the polymer mixture was left on a benchtop for ~2 months, with no special precautions taken, little to no change in the molecular weight distribution was noted.

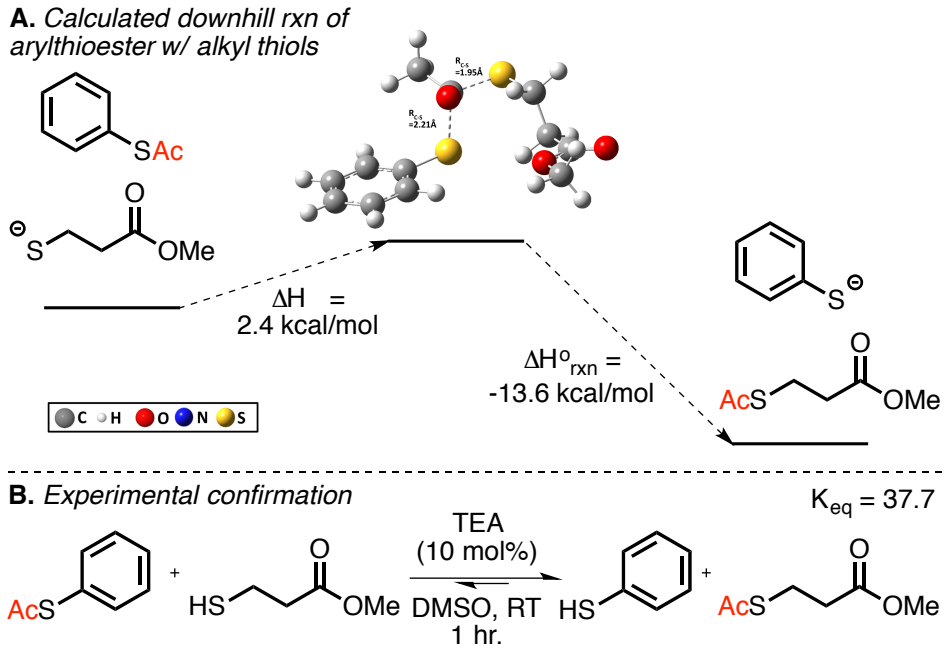


Figure 7: A. The calculated downhill reaction of arylthioesters with alkyl thiols with a minimal kinetic barrier; B. Experimental confirmation of the calculated results by NMR.

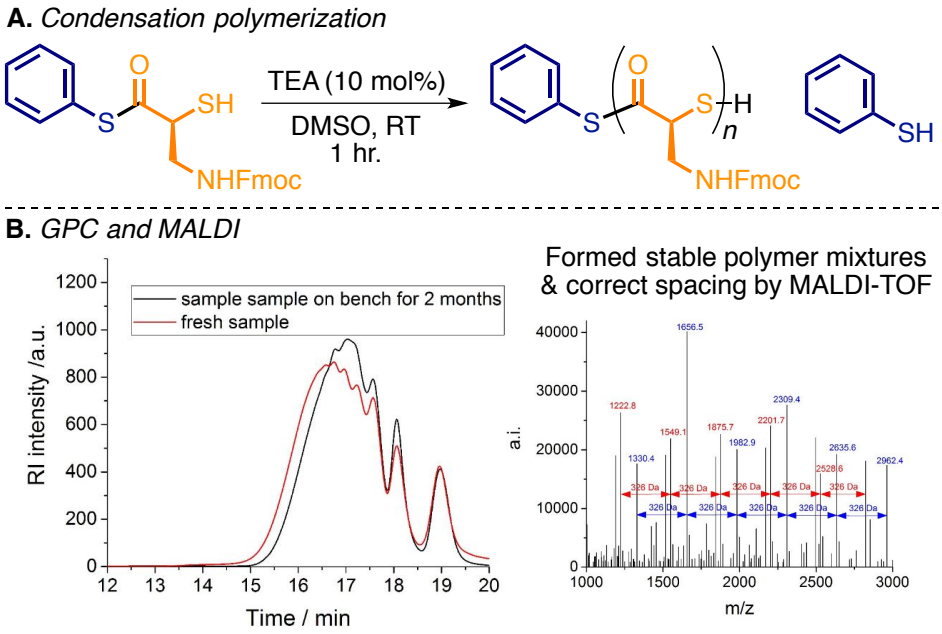


Figure 8: A. Condensation polymerization of an AB-type monomer which bears both an alkyl thiol and an aryl thioester; B. GPC and MALDI confirmation of the dynamic polythioester polymer.

f. *Synthesis of an AB-type thiol/thioester containing thymidine analogue and its polymerization*: Next, we sought to devise a synthetic route to yield significant quantities of an AB-type monomer bearing a nucleobase, free thiol, and an aryl thioester which could undergo condensation polymerization, as detailed in above section. Although there exists a gigantic amount of literature

regarding the formation of artificial DNA analogues and what dictates the strength of their binding to natural DNA, some important key points are noteworthy, such as: *i*. a 6-memebered periodicity is required, large and smaller periodicities may result in little to no binding strength; *ii*. generally uncharged polymers bind more tightly to negatively charged DNA than a polymer (such as DNA) that is negatively charged, to a point; *iii*. correct ring puckering (which is dynamic and fluxional) is extremely important and functional groups which disrupt the ability of the ring to sample various geometries (sulfones, urethanes) are deleterious towards total binding strength; and, finally, *iv.* generally speaking, the more rigid your artificial polymer is, the more tightly it will bind (if everything else held the same). Moreover, we believed that the only way we could keep the thiol and thioester from cyclizing into a thiolactone was to place them on opposite sides of a ring in different geometries, disallowing them to be in proximity of one another. Nature, obviously, employs a similar strategy, enzymatically constructing DNA's monomers from sugar units (deoxyribose). Looking into the literature, we discovered that 1-(3,5-Anhydro-2-deoxy-beta-D-threo-pentofuranosyl)thymine (or, rather, thymidine with an oxetane on the side [*top left*, **Figure 9**]) was an outstanding building block towards such AB-type polymers which would hold tightly to the guidelines for binding strongly to DNA and it is commercial and relatively inexpensive. Taking this material, we optimized a procedure developed by Yamaguchi and co-workers which impressively opens strained cyclic ethers, such as oxetanes, with alkyl lithium reagents paired with the strong Lewis acid BF_3-OEt_2 (**Figure 9**). Optimization was difficult, but conditions, as well as methods of purification, were discovered, yielding significant quantities of the ester/alcohol thymidine analogue. Acidic hydrolysis of the tert-butyl ester by formation of a lactone (by cyclization with the pendant alcohol) was performed followed by opening of the strained lactone by heating in dilute methanol, giving high yields of the methyl ester/alcohol thymidine analogue with no required purifications other than concentration. Subsequent activation of the alcohol by reaction with methanesulfonyl chloride gave methyl ester/mesyl thymidine analogue which was engaged in an S_N2-type nucleophilic displacement to invert the stereocenter. Although multiple attempts have been made to displace this secondary mesyl, finding the correct masked "SH_2" source has been challenging. Discovering a report which utilized the highly nucleophilic and easily cleavable 2,4,6-trimethoxybenzylmercaptan we immediately sought its preparation. This reagent was found to cleanly displace the mesylate, however, lower than anticipated yields were obtained; further optimization of this step continues. Subsequent basic hydrolysis of the methyl ester and formation of the aryl thioester yielded our desired, protected thymidine; again, further optimization of these steps is currently underway. Final acidic deprotection of the thiol will form our desired AB-type monomer, which, is expected to proceed quantitatively. Overall, we believe this to be the ideal route towards such molecules and are extremely excited to realize this completed synthetic route.

As can be seen in both **Figure 9** and in more detail in **Figure 10**, the minimized 3D model of the AB-type thymidine analogue shows the lack of proximity between the thiol and thioester. Thus, we anticipate that our condensation polymerization protocol will likely proceed without difficulty (**Figure 10**), forming the desired dynamic homopolymer in high conversions at room temperature. At the time of this report we are forming and polymerizing the final material to prove the validity of this approach in forming a nucleobase-functional thioester polymer.

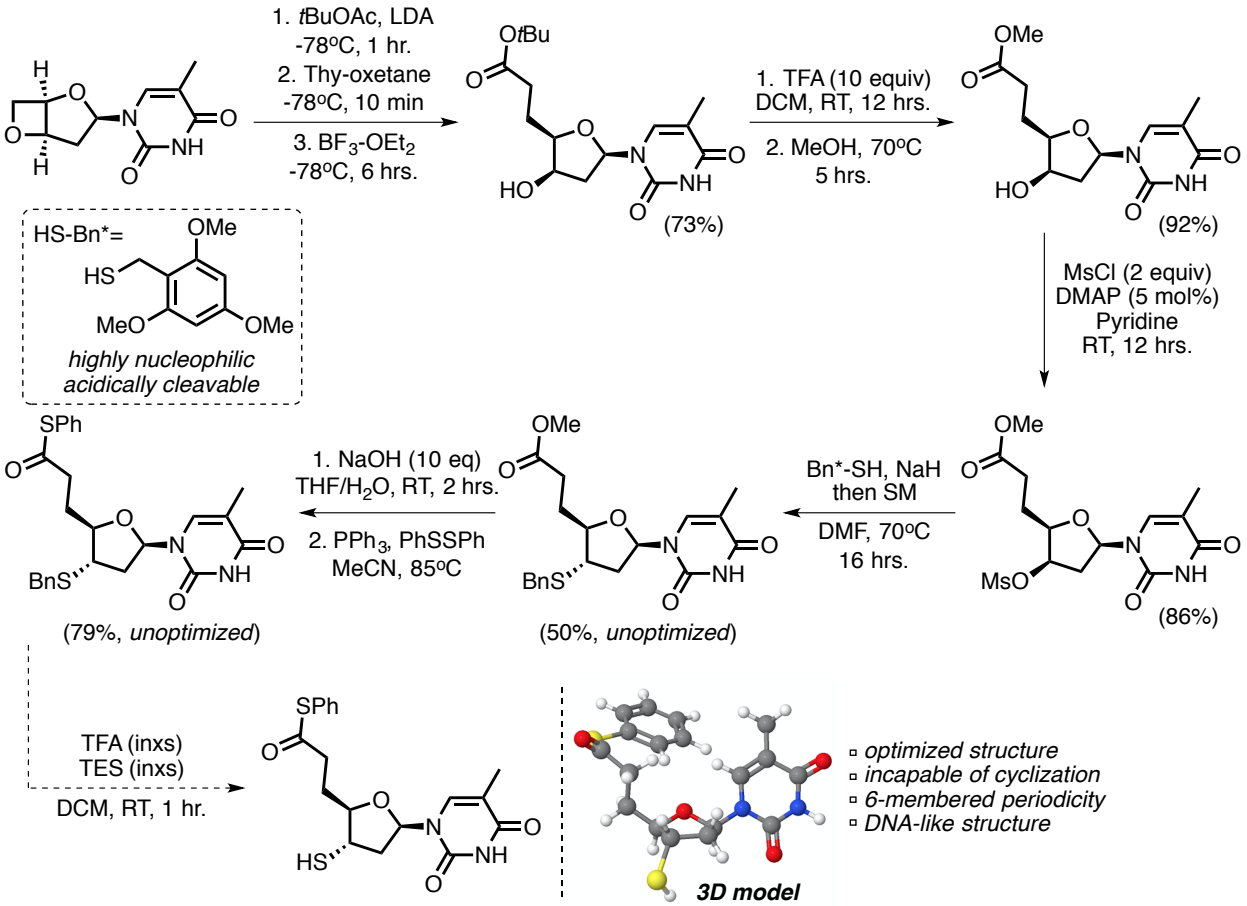


Figure 9: Synthetic route for the formation of an AB-type monomer bearing a thymine, thioester, and thiol suitable for the thiol-thioester polymerization approach described in (e).

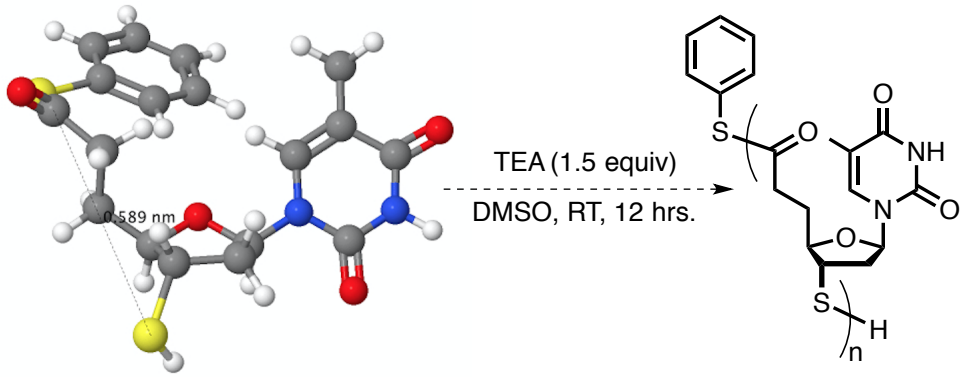


Figure 10: Condensation polymerization of the AB-type thymidine analogue with a base catalyst.

Planned Publications.

The nature of the work conducted herein is such that the manuscripts describing this effort are only now in the process of being completed. Each of the following four manuscripts will acknowledge DARPA support that was instrumental in achieving the desired outcomes. Each of these manuscripts is currently in process with planned submissions ranging from July to September of this year. Two additional publications not listed here will also likely be completed focusing on thioester-based polymers prior to the end of 2016 that will also acknowledge DARPA support.

1. Worrell, B. T.; Wang, C.; Mavila, S.; Hooi-Lim, C.; Musgrave, C.; Bowman, C. N. "A Users Guide to the Thiol-Thioester Exchange in Organic Media: Scope, Limitations, and Mechanism" *planned submission to J. Org. Chem.*, **2016**

2. Wang, C.; Worrell, B. T.; Mavila, S.; Hooi-Lim, C.; Musgrave, C.; Bowman, C. N. "A Condensation Polymerization Method Towards the Formation of Dynamic Polythioester Containing Linear Polymers" *planned submission to Macromolecules*, **2016**

3. Worrell, B. T.; Mavila, S.; Domaille, D.; Wang, C.; Hooi-Lim, C.; Musgrave, C.; Cha, J.; Bowman, C. N. "Emergent Assembly of DNA-like Monomers to Sequence Controlled Polymers" *planned submission to Science*, **2016**